THE OXIMETRIC ESTIMATION OF THIOCYANATES

BY

HOWARD WISSLER BOND

B.S., University of Arkansas, 1936
M.S., University of Illinois, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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Introduction and Historical

Many methods of analysis of thiocyanates are known. In the absence of halides, the best method is gravimetrically as the silver salt, AgSCN. In the presence of halides, there are two reliable methods: (1) volumetric, using a standard oxidizing agent which will react stoichiometrically with the thiocyanate; and (2) gravimetric, precipitating the thiocyanate as an insoluble complex, $Me(Pyridine)_{2,4}(SCN)_2$, where "Me" stands for one of the following divalent cations: zinc, cadmium, copper, cobalt, nickel, iron, or manganese. This procedure is called the Spacu procedure after its author, G. Spacu.[1]

A number of standard oxidizing agents have been proposed for the oxymetric estimation of thiocyanates, but only three of them give stoichiometric results: potassium iodate in concentrated hydrochloric acid solution[2], sodium chlorite in concentrated hydrochloric acid solution[3], and hypochlorite in the presence of the bromide ion and a sodium bicarbonate buffer.[4] The other oxidizing agents proposed give results which are higher or lower than theoretical by 2 to 6 per cent.

It was the purpose of the present research to investigate the mechanism of the oxidation of thiocyanates by hypochlorite, and to substitute homologues and derivatives of pyridine for pyridine in the Spacu procedure.

Experimental and Discussion of Results

A. The Use of Hypochlorite for the Oximetric Estimation of Thiocyanates.

Tomicek, Jasek, and Filipovic[4] demonstrated the possibility of the determination of thiocyanates by a direct titration with standard hypochlorite solution. But they determined the end point potentiometrically. The present author has shown

that certain azo dyes serve as suitable indicators for this titration.

The mechanism of the oxidation of thiocyanates by hypochlorite was investigated by means of the pH meter. To constant portions of a standard potassium thiocyanate solution, varying portions of a standardized hypochlorite solution were added. The pH of the solution was noted at ten second intervals following the addition of the hypochlorite by means of a Beckman pH meter, Industrial Model. When plotted, the readings gave straight lines for those cases in which the hypochlorite was added in less than stoichiometric portions, and curves with *two* breaks in them for those cases in which the hypochlorite was added in excess of the stoichiometric requirement. These two breaks correspond to the completion of the oxidation of thiocyanate to cyanide, and of cyanide to cyanate, respectively. Past the second break in the curves, the pH continued to decrease slowly. This can be explained on the assumption that the cyanate is slowly further oxidized to carbonate plus nitrogen, probably through the intermediate formation of formate.

B. The Use of Homologues and Derivatives of Pyridine for Pyridine in the Spacu Test.

Alpha-picoline, 8-picoline, 2,6-lutidine, 4,4′-dipyridyl, 2-bromo pyridine, 3-bromo pyridine, 3,5-dibromo pyridine, 2,6-dibromo pyridine, 2-amino pyridine, quinoline and isoquinoline, quinaldine, 6-methyl 8-nitro quinoline, and acridine were substituted for pyridine in the Spacu test for thiocyanates. It was found that if the pyridine used contained an alpha substitution of any size, no precipitates were obtained with the nickel, iron, or manganese cations; and, furthermore, if the alpha substitution were larger than methyl, no precipitates were obtained with the cadmium cation. An α,α'-dibromo substitution or an 8-nitro quinoline structure prevented the formation of precipitates with any of the seven divalent cations

tested. Steric hindrance is postulated as the basis for the phenomena experienced.

Dobbins, Markham, and Edwards[5] have proposed a scheme of analysis for the cations which depends fundamentally upon the use of pyridine plus thiocyanate as the group reagent. Group IIIB in their scheme is composed of the copper, cobalt, zinc, cadmium, nickel, and manganese divalent cations. No separations are performed on this subgroup, each cation being tested for by spot tests on separate portions. The present author has further subdivided this subgroup on the basis of the response of the six cations to thiocyanate in the presence of α-picoline and of 2,6-lutidine into three groups, composed of (1) copper, cobalt, zinc; (2) nickel, manganese; and (3) cadmium.

Summary

Azo dyes have been shown to serve as satisfactory indicators for the oximetric estimation of thiocyanates by means of standard hypochlorite solutions, replacing the former potentiometric method.

The oxidation of thiocyanates by hypochlorite has been shown to proceed stepwise, going from thiocyanate to cyanide, and from cyanide to cyanate. In the presence of excess hypochlorite the cyanate is slowly further oxidized to carbonate plus nitrogen, presumably through the intermediate formation of formate.

A modification of the Dobbins, Markham, and Edwards scheme of analysis of the cations has been devised in which use is made of the response of the cations of their Group IIIB to α-picoline and to 2,6-lutidine in the presence of thiocyanate as the basis of subdivision of the group.

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VITA

The author was born in Hugo, Oklahoma on October 31, 1916. He attended the public schools of that city and those of Fayetteville, Arkansas, and was graduated from the Fayetteville High School in June, 1932. He attended the University of Arkansas from 1932 to 1936, and was graduated in June, 1936 with a Bachelor of Science degree. In the fall of 1936 he entered the Graduate School of the University of Illinois. In June, 1938 he received the Master of Science degree. From September, 1937 to date he has held an Assistantship in Chemistry.

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